TITANIUM COPPER ALLOY HAVING EXCELLENT STRENGTH AND BENDABILITY, AND MANUFACTURING METHOD THEREOF

BACKGROUND OF THE INVENTION

Field of the Invention

The invention is related to a titanium copper alloy having excellent strength and bendability and a manufacturing method thereof.

Description of the Related Art

Excellent strength and electrical conductivity are required as fundamental properties for a copper alloy used for electrical terminals and connectors. Also, in conjunction with recent miniaturization of electronic products, miniaturization and thinness of electronic components of the products are required. Since metal materials used for such terminals or connectors are subjected to severe and complicated bending treatment, metal materials having excellent bendability are required. As for a high strength copper alloy, use of an age hardening type copper alloy is increasing recently. By applying an aging treatment to a supersaturated solid solution, fine precipitates are homogeneously dispersed in the alloy, resulting in a higher strength of the alloy. Among these age hardening type copper alloys, copper alloys containing Ti (hereinafter, referred to as "titanium copper alloys") are widely used as various kinds of terminals and connectors of electronic devices because of their excellent strength and workability.

Same as a titanium copper alloy, a beryllium copper alloy has been manufactured as a high strength copper alloy. However, a

beryllium copper alloy has such problems that beryllium compounds have toxicity and manufacturing process thereof is complicated and the production of a beryllium copper alloy entails high cost. Therefore, a titanium copper alloy having excellent strength and bendability is now in increasing demand. A titanium copper alloy obtains a high strength by precipitation of intermetallic compound particles of Cu-Ti system in a matrix in an aging treatment.

Although fine precipitates contribute to raise the strength of a titanium copper alloy, coarse precipitates do not contribute to raise the strength of the alloy. Rather, coarse precipitates in the alloy may adversely affect the performances of the alloy when the alloy is bent, coarse precipitates become starting points of cracking resulting in deterioration of bendability of the alloy. When the temperature at the solution treatment of an alloy before the aging treatment is set to be high, coarse precipitates do not appear. However, since the average grain size of the treated alloy becomes large, the treated alloy would be insufficient relating to the high strength of the quality that is recently demanded.

On the contrary, when the temperature at the solution treatment is set to be low, although the grain becomes fine, coarse precipitates remain in the matrix and it may cause detrimental effects such as, when the alloy is bent, the coarse precipitates become starting points of cracking resulting in deteriorated bendability of the alloy.

Further, with respect to the generation of coarse precipitates, there is a possibility of the coarse precipitates remaining not only in the conditions of the solution treatment before the aging treatment, but also

in the conditions of the hot rolling. The invention is intended to solve the above-mentioned problems and to provide a titanium copper alloy having excellent strength and bendability.

The present inventors have found out that; in manufacturing of a titanium copper alloy, by properly adjusting the heat treatment conditions before the hot rolling, in the end of the hot rolling and in the solution treatment in order to control precipitation of coarse precipitates which do not contribute to the strength of the alloy, the titanium copper alloy can be improved in strength and bendability.

SUMMARY OF THE INVENTION

The present invention provides (1) to (3) as follows.

(1) A titanium copper alloy having excellent strength and bendability characterized in that; it comprises 1.0 to 4.5% by mass of Ti, the balance of copper and inevitable impurities; diameters of intermetallic compound particles consisting of Cu and Ti precipitated in the alloy are 3 μm or less; the average number of the intermetallic compound particles having the diameters of 0.2 to 3 μm is 700 or less, preferably 6 to 700 per a cross-sectional area of 1000 μm^2 in a transverse direction to a rolling direction; the average grain size measured in a cross-sectional area in a transverse direction to a rolling direction is 10 μm or less; and a tensile strength is 890 MPa or more.

(2) A manufacturing method of the titanium copper alloy according to the above (1) comprising a hot rolling, a (first) cold rolling, a solution treatment, a (second) cold rolling and an aging treatment, of a titanium copper alloy ingot in this order characterized in that;

the ingot is heated at a temperature of 850 to 950 °C for 30 minutes or more before the hot rolling and then the ingot is hot rolled and the temperature in the end of the hot rolling is 700 °C or more;

in the solution treatment, the material is annealed at a temperature in a range between (T-50) °C and (T+10) °C, wherein T is a temperature at which the solubility of Ti in Cu is equal to the concentration of Ti contained in the alloy; and thereafter the annealed material is cooled at a cooling rate of 100 °C/sec or more.

(3) A manufacturing method of the titanium copper alloy according to the above (2), wherein a reduction ratio in the second cold rolling is 50% or less.

BRIEF DESCRIPTION OF DRAWINGS

Figure 1 shows a phase diagram of Cu-Ti system (Experimental data on the Ti-Cu stable equilibrium (Cu) solvus, coherent solvus, and spinodal).

The above-mentioned Cu-Ti phase diagram in Figure 1 is quoted from "Phase Diagrams of Binary Copper Alloys" by P.R.Subramanian, D.J.Chakrabarti and D.E.Laughlin, ASM International, pp447-460 (1994).

The temperature T °C at which the solubility of Ti in Cu is equal to the concentration of Ti contained in the alloy is a temperature on a solvus (solid solubility) shown in Figure 1. Illustratively, when the concentration of Ti is 2.6% by mass, T °C is 755°C.

DETAILED DESCRIPTION OF THE INVENTION

Hereinbelow, the present invention is described in detail.

(i) The concentration of Ti

Ti is characterized in that it induces spinodal decomposition in the aging treatment of a titanium copper alloy, thereby generating a modulated structure in the alloy, and ensuring very high strength of the alloy. However, if the concentration of titanium is less than 1.0% by mass, reinforcement of the alloy caused by the aging treatment cannot be expected. Conversely, if the concentration of titanium exceeds 4.5% by mass, precipitation is likely to occur in a grain boundary in the aging treatment, thus the strength of the alloy may be lowered and cracking may occur in the grain boundary when the alloy is bent. From the above, the concentration of titanium in the alloy should be 1.0 to 4.5% by mass. Further, in addition to the alloy, such as chromium, zirconium, nickel and iron may be added in a total amount of 1.0% by mass or less so as to have the same effect as that of titanium.

(ii) Intermetallic compound particles of Cu and Ti precipitated in the matrix

In a titanium copper alloy, high strength can be achieved by precipitation of the intermetallic compound particles of Cu and Ti in the matrix. However, the intermetallic compound particles of Cu and Ti contributing to excellent strength of the alloy are fine particles having the diameters of less than 0.2μm. The intermetallic compound particles having the diameters of 0.2μm or more do not contribute to excellent strength but become starting points of cracking when the alloy is bent. Especially, the intermetallic compound particles having the diameters of more than 3μm cause extraordinary impaired bendability.

Thus, it is necessary that the diameter of the intermetallic compound particles is set to be 3μm or less. Further, the inventors have found that even the intermetallic compound particles having the diameters of 0.2 to 3 μm adversely affect bendability of the alloy when the number of particles is more than 700 per a cross-sectional area of 1000 μm^2 in a transverse direction to a rolling direction. Accordingly, the diameter of the intermetallic compound particles of Cu and Ti precipitated in the matrix should be 3μm or less, and the average number of the intermetallic compound particles having the diameters of 0.2 to 3 μm should be 700 or less per a cross-sectional area of 1000 μm^2 in a transverse direction to a rolling direction. Here, the composition of an intermetallic compound of Cu and Ti is $Cu_{3\text{-}4}Ti$.

On the other hand, in punch press-work, since the intermetallic compound particles of Cu and Ti having the diameters of 0.2 to 3 μm promote transmission of cracking in the alloy which eventually prevent a press mold wearing. Therefore, the presence of the intermetallic compound particles having the diameters of 0.2 to 3 μm in the average number of 6 or more per a cross-sectional area of 1000 μm^2 in a transverse direction to a rolling direction imparts long-life to the press mold to be used. From the above, the average number of the intermetallic compound particles having the diameters of 0.2 to 3 μm is preferably 6 to 700 per a cross-sectional area of 1000 μm^2 in a transverse direction to a rolling direction.

(iii) Average grain size

The grain size of a titanium copper alloy affects strength and bendability of the alloy largely. The grain having a size of more than

10μm disables to obtain the desired strength. Adversely, when the alloy having an average grain size of more than 10μm is bent in the process, roughness is likely to occur on the alloy surface. Thus, the average grain size should be 10 μm or less. Here, measurement of the average grain size is carried out by exposing a structure of a cross-sectional area of a specimen alloy in a transverse direction to a rolling direction by means of etching (water (100mL)-$FeCl_3$ (5g)-HCl (10mL)) and by obtaining an average grain size by means of an intercept method according to JIS H 0501.

(iv) Manufacturing method

In the manufacturing method of a titanium copper alloy of the invention, a hot rolling, a first cold rolling, a solution treatment, a second cold rolling and an aging treatment, of a titanium copper alloy ingot are conducted in this order. Further, after the first cold rolling, annealing may be carried out for the purpose of recrystalization, and then a further cold rolling and a solution treatment can be conducted in this order. The manufacturing method of the invention is described in detail below.

(a) Hot rolling

In general, manufacturing of a titanium copper alloy ingot is carried out by semi-continuous casting process. In solidification step at the casting, coarse intermetallic compound particles of Cu-Ti system may occur in the matrix. The occurred coarse intermetallic compound particles would be solved in the matrix so as to form a solid solution by heating at a temperature of 850°C or more for 30 minutes or more and the subsequent hot rolling wherein the temperature in the end of the

hot rolling should be 700 °C or more. However, when the temperature before the hot rolling exceeds 950°C, stubborn scale occurs on the material surface, becoming the reason of cracking in rolling and bad yields owing to removal of the scale. Accordingly, the temperature before the hot rolling should be between 850°C and 950°C.

(b) Solution treatment

In order to obtain homogeneously dispersed fine intermetallic compound particles of Cu and Ti, the solution treatment is commonly conducted at a temperature on or above the solvus shown in Figure 1; specifically, at or above the temperature at which the solubility of Ti in Cu is equal to the concentration of Ti contained in the alloy. However, high annealing temperature promotes the grain growth resulting in insufficient strength and/or bendability. In the invention, so as to obtain an average grain size of 10 μm or less, it is necessary to anneal at a temperature of (T+10)°C or less, wherein T is a temperature at which the solubility of Ti in Cu is equal to the concentration of Ti contained in the alloy. Further, when the temperature in the solution treatment is less than (T-50)°C, Ti would not form solid solution with Cu resulting in the number of the intermetallic compound particles of Cu and Ti being out of the range of the invention. Accordingly, the solution treatment should be carried out at a temperature in the range between (T-50)°C and (T+10)°C. Further, when a cooling rate of the annealed alloy is not more than 100°C/s, precipitation of the intermetallic compound particles would occur in the grain boundary in the alloy. The precipitation of the intermetallic compound particles may cause cracking in the grain boundary when the alloy is subjected

to a bending stress, and accordingly the cooling rate in the solution treatment should be 100°C/s or more. The cooling method is not particularly limited in the invention.

(c) Second cold rolling

In order to obtain the high strength alloy, a reduction ratio in the second cold rolling after the solution treatment is preferably high. However, since when a reduction ratio is more than 50 %, work hardening of the alloy is excessive, texture of the alloy caused by the rolling is developed too much, thus bendability in a transverse direction to a rolling direction deteriorates remarkably. For this reason, a reduction ratio is preferably 50% or less in the second cold rolling. Further, when the Ti content is about 3% by mass, the titanium copper alloy having excellent strength, such as 890 MPa or more of a tensile strength, can be obtained at a reduction ratio of about 10% or more.

Here, assuming that the thickness of the alloy plate before the cold rolling is t_0 and the thickness of the alloy sheet after the cold rolling is t, the reduction ratio X of the cold rolling is defined as:

$$X=(t_0-t)/t_0 \times 100(\%).$$

(d) Aging treatment

The aging treatment of the titanium copper alloy is suitably conducted at a temperature of 300 to 600°C in the invention in order to obtain the desired strength and electrical conductivity.

EXAMPLES

Firstly, using electrolytic copper or oxygen-free copper as a raw material, copper alloy ingots (20 mm thick x 100 mm wide x 200 mm

long) of the various compositions shown in Table 1 were obtained by melting and casting in a high frequency vacuum melting furnace. Subsequently, each ingot was heated and hot rolled at a temperature described in Table 1 to obtain a plate having a thickness of 8 mm. The scale on the surface of the plate was removed and polished, then the first cold rolling was carried out to obtain a sheet having a thickness of 0.43 mm. In the subsequent solution treatment, each sheet was annealed for 30 minutes at a temperature and cooled to the room temperature at a cooling rate described in Table 1.

Then the second cold rolling was carried out at a reduction ratio of 30% to obtain each sheet having a thickness of 0.3 mm, followed by the aging treatment under conditions at which it is able to obtain the highest strength for each specimen alloys. In example 9, the reduction ratio in the second cold rolling was set to be 60 % in order to observe the effect of a reduction ratio on bendability of the alloy.

For each alloy obtained from the above, various properties were measured. Tensile strength was evaluated using a tensile tester according to JIS Z 2241. Bending test of specimens was conducted according to W bending test (JIS H 3130) under a condition that bending radius/thickness of a sheet is 2. The convex part on the surface of the specimen made by bending was observed by an optical microscope. The evaluation standard of bendability of the alloy was classified in three ranks: rank O; no wrinkle was observed, rank Δ; large wrinkles was observed, rank X; a cracking occurred.

In measurement of the average grain size, a structure of a cross-sectional area of a specimen alloy in a transverse direction to the rolling

direction was exposed by means of etching (water (100mL)-$FeCl_3$(5g)-HCl(10mL)) and an average grain size was measured by means of the intercept method according to JIS H 0501. In the intercept method, an average grain size in a direction of sheet-thickness and an average grain size of sheet-width were obtained by measuring the exposed structure. Then the average value of these two average grain sizes was calculated and referred to as "the average grain size" of the alloy. As for the observation of the intermetallic compound particles of Cu and Ti precipitated in the alloy, a cross-sectional area of the alloy in a transverse direction to the rolling direction was polished by use of a water-proof sand paper of #150, followed by further polishing so as to obtain mirror finished surface by use of a finishing abrasive in which colloidal silica having a particle diameter of 40 nm is suspended. Then carbon vapor deposition was carried out on the polished alloy specimen and a reflected electron image obtained by use of FE-SEM (scanning electron microscope) (XL30SFEG, manufactured by FEI Company Japan) was observed. The scanning field was 1000 μm^2 and 5 fields each having different visions were observed for each alloy. As for the evaluation of diameters of the intermetallic compound particles in table 1, the minimum diameter of a circle containing each intermetallic compound particle of Cu and Ti in the observation field was actually measured and a specimen containing intermetallic compound particles having the diameters of more than 3μm was evaluated as "X". On the other hand, a specimen containing no intermetallic compound particle having a diameter of more than 3μm was evaluated as "O". The number of the intermetallic compound particles was obtained as the

averaged number of the intermetallic compound particles of Cu and Ti observed in 5 fields.

Table 1 (to be continued)

Example No.	1	2	3	4	5	6	7	8	9
Concentration of Ti (mass %)	1.1	2.8	4.1	3.8	1.8	4.5	3.4	2.6	2.6
Temperature before the hot rolling (°C)	860	875	850	900	855	870	880	860	860
Temperature in the end of the hot rolling (°C)	750	740	700	770	710	740	730	725	725
Temperature (T) of a solvus in a phase diagram (°C)	640	767	834	820	701	852	800	755	755
Annealing Temp. in the solution treatment (°C)	650	750	835	817	700	820	805	750	750
Cooling rate in the solution treatment (°C/s)	120	200	120	100	115	150	105	180	180
Reduction ratio in the second cold rolling (%)	30	30	30	30	30	30	30	30	60
Tensile strength (MPa)	915	989	1054	1034	936	1096	1004	954	1001
Bendability	O	O	O	O	O	O	O	O	△
Average grain size (μm)	4	2	8	5	4	3	6	5	4
Diameter of precipitates (≤3μm)	O	O	O	O	O	O	O	O	O
Number of precipitates (≤700)	7	362	264	378	49	546	330	309	314

Table 1 (continued)

Comparative Example No.	1	2	3	4	5	6	7	8	9
Concentration of Ti (mass %)	0.8	0.5	5.0	4.8	2.8	3.1	3.4	2.6	2.6
Temperature before the hot rolling (°C)	850	880	870	890	830	850	875	860	860
Temperature in the end of the hot rolling (°C)	710	730	730	750	710	675	730	725	725
Temperature (T) of a solvus in a phase diagram (°C)	606	560	874	866	767	784	800	755	755
Annealing Temp. in the solution treatment (°C)	610	565	850	840	760	790	810	700	800
Cooling rate in the solution treatment (°C/s)	110	130	100	170	150	120	80	180	180
Reduction ratio in the second cold rolling (%)	30	30	30	30	30	30	30	30	30
Tensile strength (MPa)	830	815	879	868	913	940	926	932	870
Bendability	O	O	X	X	X	X	X	X	O
Average grain size (μm)	5	5	3	3	4	6	4	1	35
Diameter of precipitates (≤3μm)	O	O	O	O	X	X	X	X	O
Number of precipitates (≤700)	5	5	1583	894	659	1177	1428	1219	43

As can be seen from Table 1, the Example specimens of the invention had excellent strength and bendability. Besides, in Example No.9, the composition of the alloy, the temperature before the hot rolling, the temperature in the end of the hot rolling, the annealing temperature in the solution treatment, and the cooling rate after the solution treatment were the same as in Example No.8 and the reduction ratio was out of the range specified in the above mode (3) of the invention. The specimen of Example No. 9 was even though excellent in tensile strength but inferior in bendability to some extent to that of Example No. 8.

On the contrary, in Comparative Examples 1 and 2, since the concentrations of Ti were less than the lower limit of the above mode (1), the strength of these specimens was insufficient. Further, in Comparative Examples 3 and 4, since the concentration of Ti exceeded the upper limit of the above mode (1), precipitation of the intermetallic compound particles of Cu and Ti occurred in the grain boundary causing poor strength of the alloys. Also, in Comparative Examples 3 and 4, although the coarse intermetallic compound particles having the diameters of 3μm or more were not present, the number of the intermetallic compound particles having the diameters of 0.2 to 3 μm exceeded the upper limit of the above mode (1) resulting in poor bendability.

Since, in Comparative Example 5 the temperature before the hot rolling was less than the lower limit of the above mode (2), in Comparative Example 6 the temperature in the end of the hot rolling was less than the lower limit of the above mode (2), and in Comparative

Example 7 the cooling rate after the solution treatment was less than the lower limit of the above mode (2), the coarse intermetallic compound particles having the diameters of 3μm or more were present in the specimens of these Comparative Examples. Further, in Comparative Examples 6 and 7, since the number of the intermetallic compound particles having the diameters of 0.2 to 3μm was 700 or more, bendability was poor in these Comparative Examples.

Furthermore, in Comparative Examples 8 and 9, the composition of the alloy, the temperature before the hot rolling, the temperature in the end of the hot rolling, the cooling rate after the solution treatment, and a reduction ratio in the second cold rolling were the same as in Example No.8 and the annealing temperature in the solution treatment was out of the range specified in the above mode (2). In Comparative Example 8, since the temperature in the solution treatment was low and Ti was not solved completely into Cu in the solution treatment, the coarse intermetallic compound particles having the diameters of 3μm or more was present and the number of the intermetallic compound particles having the diameters of 0.2 to 3 μm was 700 or more resulting in poor bendability. Further, in Comparative Example 8, when the tensile test was conducted, the intermetallic compound particles became starting points of fracture, thus the tensile strength was inferior to that of Example 8. In Comparative Example 9, since the temperature in the solution treatment was high, the grain grew large and the tensile strength was inferior to that of Example 8.

As can be seen from the above description, in the invention, by adjusting heat processing conditions before the hot rolling, in the end of

the hot rolling and in the solution treatment of titanium copper alloy manufacturing method, and control this precipitation of coarse precipitates which do not contribute to the strength, the strength and bendability of a titanium copper alloy are improved and it is possible to provide a copper alloy excellent in strength and bendability which can be consistent with miniaturization of electronic components.